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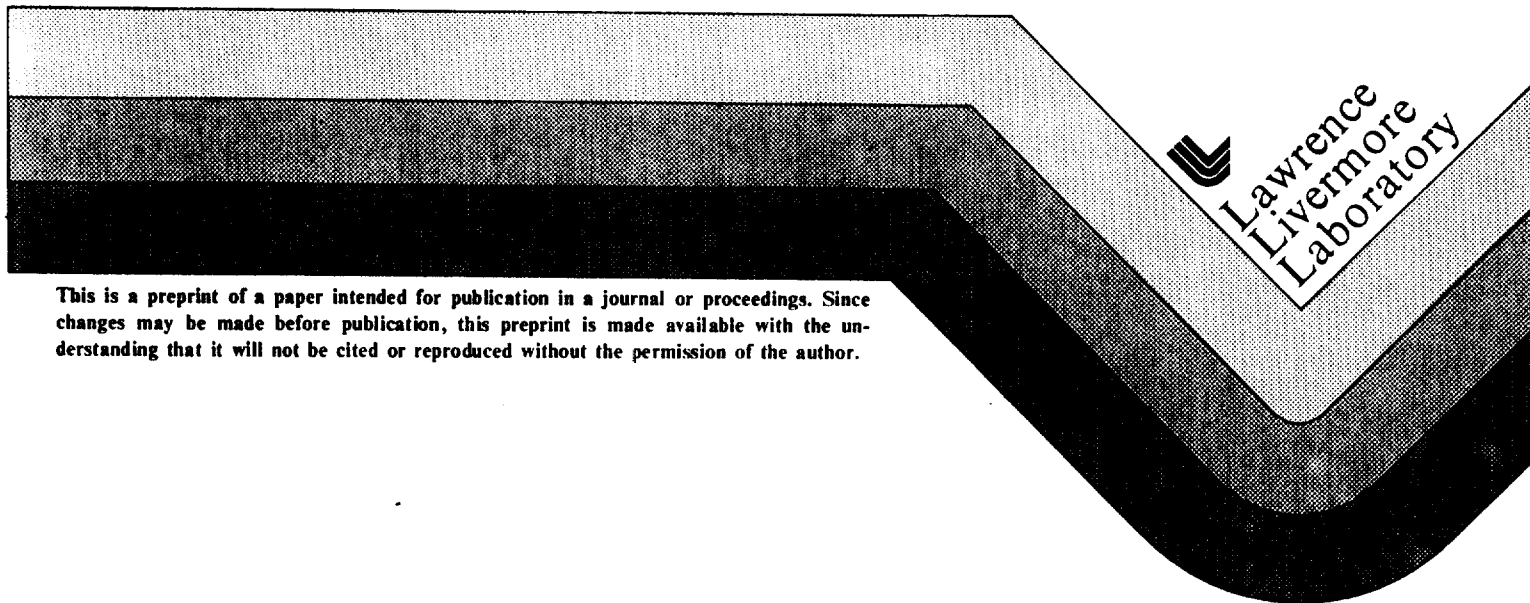
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THE EFFECT OF A HEATED ATMOSPHERE ON THE EMITTANCE OF BLACK CHROME SOLAR COLLECTOR PIPE SURFACES[†]

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ABSTRACT

The total hemispherical emittance of the surfaces of solar collector pipes was measured in the temperature range 100-300°C before and after exposure to a heated humid or dry air atmosphere. The first exposure to heated air lowered the emittance of black chrome surfaces about 20%. Similar exposure increased the emittance of bare steel significantly, but had no effect on a nickel surface. Subsequent exposures to heated dry or humid air lowered the emittance of the black chrome surfaces by lesser amounts, in what appeared to be a limiting process. In all cases, the emittance of the black chrome surfaces increased strongly with temperature.

A possible explanation for the lowering of the black chrome emittance is the oxidation and subsequent outgassing of carbon contaminants in the black chrome coating. However, sufficient microscopic evidence to verify this hypothesis is not available.

1. INTRODUCTION

An understanding of environmental effects on the radiative properties of surfaces used in solar collectors can be important in estimating their long-term thermal efficiencies. An investigation of the effect of exposure to heated moist or dry air on black chrome surfaces was therefore undertaken. This used an apparatus designed to measure the total hemispherical emittance of pipes of length suitable for use in a prototype solar collector. (1,2) The method used is a steady-state, calorimetric one, capable of measuring emittance as a function of temperature. The large sample size distinguishes it from the usual calorimetric measurements of small, flat samples. Since this method is limited to large samples, it complements rather than replaces the other methods.

The generally-accepted theory for the performance of a composite selective surface requires that the absorptive layer be thick enough to absorb most of the radiation in the solar spectrum, but thin enough to be largely transparent to infrared radiation so that the emittance is primarily that of the metal substrate. If the absorptive layer is too thick, the absorptance is not significantly affected, but the emittance is increased. (3,4)

Black chrome has a complex microscopic structure. (3) Small chromium particles (e.g., ~ 140 Å) are surrounded by a matrix of chromium oxides, predominately Cr₂O₃. These amorphous mixtures of metal and semiconductor form particles ranging from about 500 to 3000 Å that make up a low-density structure. The chromium fraction increases from the outer surface inward, from about 50% to as much as 90%. A thickness of a micron or less is desired for solar applications to allow the low emittance of the metallic substrate to dominate.

Various theories have been developed that attempt to explain the optical properties of selective surfaces. (5,6) So far, however, it appears that actual selective surfaces are too complicated to be treated with success. Even the preparation of surfaces of known properties to allow comparison with the theories has not been very successful. Therefore for applications, the need for emittance measurements will exist for some time.

2. Experimental Apparatus

A schematic of the apparatus is shown in Fig. 1. (See Ref. 1 for details.) The emittance of the test pipe, ϵ_1 , is given approximately by

$$\frac{1}{\epsilon_1} = \frac{A_1 \sigma (T_1^4 - T_2^4)}{P_{\text{net}}} - \frac{D_1}{D_2} \left(\frac{1}{\epsilon_2} - 1 \right) \quad (1)$$

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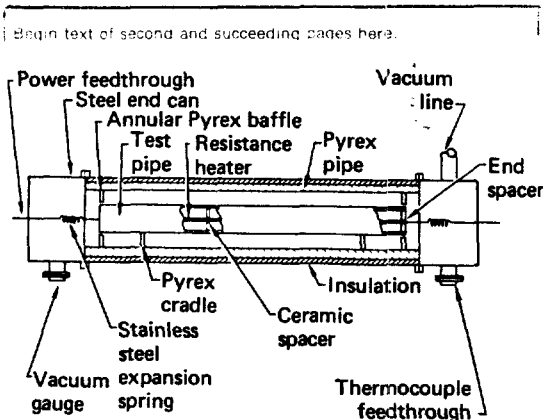


Fig. 1: Schematic of emittance apparatus. The inner diameter of the Pyrex pipe was 15.2 cm, and a typical test pipe was 4.4 cm o.d. and 343 cm long.

where ϵ_2 is the emittance of the outer Pyrex glass pipe ($\epsilon_2 \approx 0.85$), A_1 , D_1 and T_1 are the area, outer diameter and temperature of the test pipe, D_2 and T_2 are the inner diameter of the Pyrex pipe and its temperature, σ is the Stefan-Boltzmann constant, and P_{net} is the net power radiated by the test pipe. P_{net} is calculated by subtracting the power lost by other paths from the gross power into the resistance heater. Equation (1) is for infinite, concentric, isothermal cylinders. However, it agrees to within 1% with finite-element calculations that account for the empirically-observed temperature gradient on the ends of the test pipe, provided T_1 is replaced by an area-weighted average temperature. (1)

Use of this apparatus to study the effects of heating and exposure to an atmosphere brings with it advantages and limitations similar to those for the emittance measurements themselves. Tests on small samples can be better controlled and the samples can be better characterized, but such work does not yield results directly applicable to coatings on actual pipes. With this apparatus, data can be obtained on pipes at the expected operating conditions.

3. Test Program

Since many solar absorber surfaces are exposed to the ambient atmosphere, there are many exposure conditions of interest. For this initial study, it was decided to place more emphasis on producing observable effects rather than attempting the much more difficult task of explaining changes in emittance in terms of changes in microscopic structure.

The surfaces were plated on 4.4 cm diameter mild steel pipes using the Harshaw black chrome process. The conditions specified to the plater were two pipes with 0.7 μm black chrome over 12.7 μm nickel on steel, one pipe with 0.7 μm black chrome over 12.7 μm hard chrome on steel, and one with 12.7 μm nickel on steel. These thicknesses were strictly nominal as there is generally no way of measuring thickness during the plating process. No measurements of coating thicknesses on the test pipes were made. The black chrome on nickel surfaces were described as the "optimum solar coating" by the plater. In addition, one unplated steel pipe was subjected to the standard test sequence as a reference.

Test surfaces were exposed to heated, humid air for about 65 hours. This period proved sufficient to oxidize the bare steel pipe and increase its emittance significantly.

The standard test sequence was the following:

1. Measure ϵ in vacuum at 4-6 pipe temperatures.
2. Introduce water vapor to the system at ambient temperature, add dry air to give 8% water vapor. (This meant, for example, 18.7 torr water vapor and a total pressure of 234 torr.) This corresponds to 100% relative humidity at 40°C.
3. Heat system to about 260°C for a total time (including heat-up) of about 65 hours.
4. Repeat Step 1. Some pipes were subjected to additional baking in dry air (same total pressure, no water vapor) and subsequent measurements of $\epsilon(T)$; one pipe was baked twice after exposure, then exposed a second time to heated, humid air.

4. DISCUSSION OF RESULTS

A straight line fit to the data from each series of runs was calculated by the method of least squares. (1) The results are shown in Figs. 2-4. The line parameters are given in Table 1. The error bars in the figures are the random errors calculated for each data point. The scatter of the data about the lines is much less than the error bands. Thus the linear relationship of emittance and temperature, over the limited temperature range studied, is well established, with the possible exception of the nickel-plated pipe.

The importance of accounting for the temperature dependence of the emittance when designing solar collector systems is evident from these results. A surface with an acceptable emittance (e.g., 0.10) at ambient temperature may not be acceptable if operated at 600°K with $\epsilon = 0.35$.

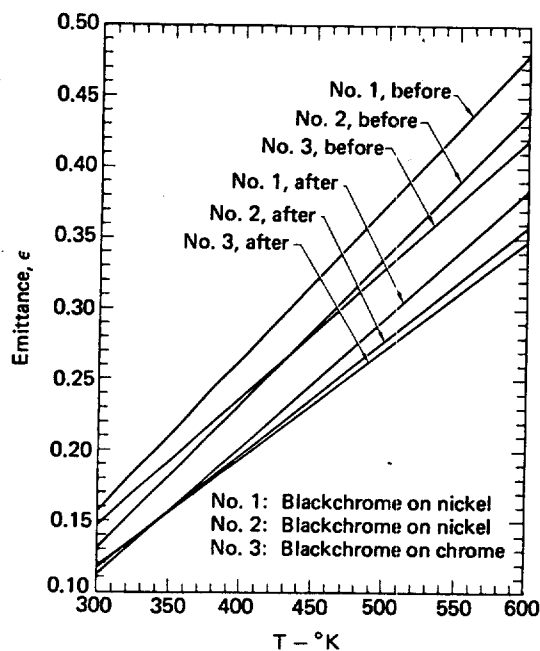


Fig. 2: Comparison of the three black chrome surfaces before and after the first exposure to heated, humid air.

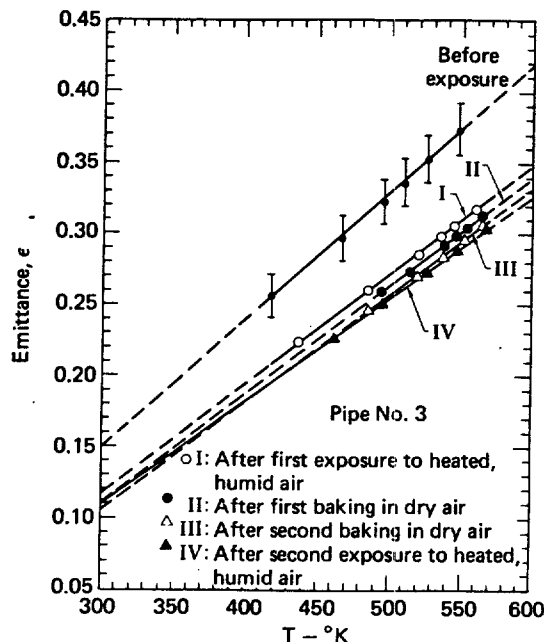


Fig. 3: Emittance of black chrome on a bright chrome substrate before and after repeated exposures to dry and humid air.

The slope of emittance versus temperature (i.e., the coefficient "B" in Table 1) is typically of the order of $1-2 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$ for most metals. The actual value depends on the location and shape of the transition from high to low emittance. The temperature dependence of black chrome emittance was investigated analytically using a representative spectral reflectance curve for black chrome. The results indicated that the major factor in determining the slope of black chrome in the temperature range of interest is simply the temperature dependence of the blackbody distribution.

The most remarkable result evident in Fig. 3 is that exposure to a heated air atmosphere (moist or dry) always lowered the emittance of black chrome. Two points should not be overlooked, however. One is that the exposure was not extreme in duration, nor was it severe in terms of temperature or relative humidity (when heated), especially considering possible exposures of pipes used in highly concentrating solar systems. The other point is that other measurements (on small sections cut from test pipes) indicated that the solar absorptance also decreased, an important result for the thermal efficiency of the collector.

The emittance of the bare steel pipe, which was visibly oxidized after one test sequence, increased as expected. A commercially-galvanized steel pipe (data not shown) also showed a significant increase in emittance after exposure.

Table 1: Line Parameters Before and After Exposure to Heated Air

$$\epsilon(T) = A + BT$$

A
($10^{-4} \text{ } ^\circ\text{K}^{-1}$) COMMENTS

-.027	2.25	nickel, before exposure
-.005	1.77	after exposure to humid air
.146	1.92	bare steel, before exposure
-.202	11.7	after exposure to humid air
-.166	10.8	No. 1 (bc/nickel) before
-.161	9.09	after exposure to humid air
-.178	10.3	No. 2 (bc/nickel), before
-.126	8.08	after exposure to humid air
-.148	8.32	after exposure and after baking in dry air
-.125	9.09	No. 3 (bc/chrome), before
-.118	7.79	after exposure to humid air
-.122	7.72	after baking in dry air
-.126	7.65	after second baking
-.112	7.32	after two bakings, second exposure to humid air

Typical relative errors from least squares method: B ($\pm 2\%$, except for nickel, $\pm 7\%$); A ($\pm 7\%$, except nickel, $\pm 60\%$); maximum relative error in ϵ ($\pm 2-3\%$).

The low pre-exposure emittance for the nickel (Fig. 4) compared to the pre-exposure results for the black chrome pipes indicates that the substrate did not determine the emittance. The most likely explanation for this is that the black chrome was too thick. Not only does increased thickness lead to increased emittance, but the slope also increases. (7) The slope of ϵ versus T for all the black chrome pipes was at least 10% lower after the first exposure to a heated atmosphere.

It was originally expected that exposure to hot, humid air would cause oxidation of some of the chromium in the black chrome, or at least adsorption of water vapor. Either of these changes was expected to increase the emittance, although this conclusion is certainly model-dependent.

Electron spectroscopy for chemical analysis performed on small test coupons attached to some of the test pipes did not show any evidence of the oxidation of the chromium. Only Cr_2O_3 was observed before and after exposure. ESCA only observes the first 5-7 atom layers, so changes in stoichiometry, morphology and crystallization remain possibilities. Scanning electron microscopy showed removal of surface debris, but no significant changes.

The possibility that adsorption of water might occur due to exposure to a heated, humid atmosphere was eliminated by a concurrent black chrome outgassing study. (8) This showed that water vapor was driven off rather than adsorbed at ambient and elevated temperatures.

More importantly, no change in emittance was observed for a black chrome pipe used for preliminary runs and heated in vacuum for several months prior to its first exposure to a heated atmosphere. By contrast, a pipe that had been painted with a high-temperature black paint outgassed considerably when heated in vacuum and showed a definite sharp decrease in emittance after reaching outgassing equilibrium.

Since heating in either moist or dry air produced an initial large (16-20%) decrease in emittance, and the decreases approach a limiting value upon subsequent heating in air, the possibility of a reaction with oxygen suggests itself. This could be by the formation of CO or CO_2 from the carbon in the organic acids and additives used in the plating process.

The presence of a dielectric such as carbon or its compounds would be expected to increase the emittance of any low-emittance surface. Such contaminants might also contribute to the high solar absorptance. Their subsequent removal should therefore lower both emittance and absorptance, as observed. An alternative

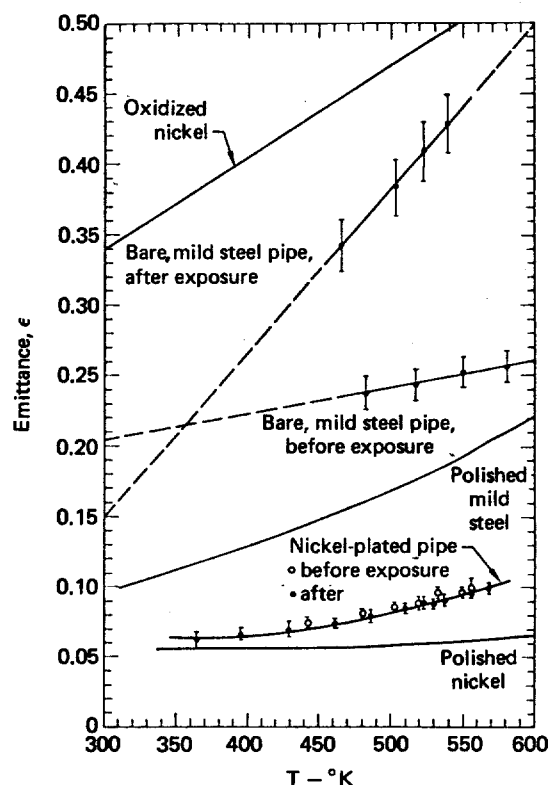


Fig. 4: Emittance of bare steel and nickel-plated pipes before and after exposure to heated, humid air. Published data for polished mild steel and oxidized nickel are from (10); published data for oxidized steel is too high to show on this plot.

way of describing the observations is that exposure to heated air somehow makes a black chrome layer, which was initially too thick optically, more transparent in the infrared, allowing the metal substrate to become more of a factor in the emittance. A reduction in the infrared absorptance of the black chrome would reduce the solar absorptance slightly. If, on the other hand, the black chrome layer were of optimum thickness, the emittance would be controlled much more by the substrate and driving off of carbon should not lower the emittance as much.

Carbon is a known, although generally neglected, contaminant of plated black chrome. A recent study of outgassing of black chrome showed considerable amounts of carbon and its oxides. (8) This was for black chrome plated by the DuPont process. Black chrome plated by the Harshaw Chemical process (used for our test pipes) is however, believed to contain less carbon than DuPont black chrome.

Questions remain about the quantity of carbon required to account for these effects, as well as its form and location in the coating. Auger sputtering suggests that carbon may be as much as a few percent of some black chrome coatings. (9) Also, it is still difficult to explain the need for an atmosphere, as Beat observed considerable outgassing of carbon even at ambient temperature for DuPont black chrome. (8)

Lampert's work on the effect of heating on emittance and absorptance showed significant reduction in both properties after heating for 100 hours at 300°C, both in vacuum and in dry air. (3) His samples were thinner (0.5 micron) than the coatings on our pipes. This may have facilitated the oxidation of carbon by trapped oxygen and its subsequent removal even when heated in vacuum.

5. CONCLUSIONS

- The total hemispherical emittance of the black chrome surfaces studied increased strongly with temperature.
- Heating in vacuum at temperatures to 270°C for hundreds of hours did not significantly change the emittance of the black chrome coatings studied.
- A first heating in moist (8%) or dry air at 260°C for about 65 hours lowered the emittance of black chrome significantly (e.g., as much as 20%); subsequent exposures to such a heated atmosphere lowered the emittance less and less, approaching a limiting line.
- The mechanism for this decrease in emittance is not clear. It appears by its nature to be the result of an outgassing or other limiting process. The requirement for air suggests oxidation of a contaminant; carbon appears to be the most likely one. An alternate, or possibly concurrent, process may involve changes in the black chrome structure. Additional work on a microscopic level is necessary.

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